Oxygen plasma treated super-hydrophobic nozzle for electro-spray device

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ABSTRACT

In this study, electro-spray device with super-hydrophobic nozzle is presented and fabricated instead of protruded nozzle. The super-hydrophobic nozzle is created by roughening the surface of the polyfluorotetraethylene (PTFE) or Teflon coated surface by argon and oxygen plasma treatment. We present a simple process of fabricating super-hydrophobic nozzle which is able to allow itself to enhance the stability of liquid meniscus at the outlet of the nozzle. Through the ion beam treated nozzle, the liquid does not overflow and keeps more stable and repeatable ejection of liquid jet.

Keywords: Ion beam treatment, Super-hydrophobic surface, Electro-spray

1 INTRODUCTION

Electro-hydrodynamic spraying, or electro-spray, has been a subject of intensive research in recent years; for instance, mass spectrometry [1]-[3], printing technology [4]-[6], and biological micro-arrays [7]. As a mechanism that allows for the dispersal of very fine liquid droplets, its potential applications are seen as numerous. When a low, constant flow rate of a liquid is passed through a capillary, and the meniscus of the liquid subject to an electric field beyond certain strength, an electric charge is induced on the meniscus, and a combination of electrostatic, hydrostatic, and capillary forces elongate the liquid into a conical form known as a Taylor-cone [8]-[10].

Depending on the flow rate of the liquid and the electric field applied, these cones emit fine particles in a variety of classified regimes or modes, one of which is known as the "cone-jet" mode. This cone-jet spraying mode, in which a steady jet of charged droplets is emitted from the apex of the Taylor-cone, allows for spray drops in the sub-micron range [10]. This emission of charged droplets is properly termed "electro-spray" [9].

Conventional inkjetting devices based on thermal bubble or piezoelectric pumping, however, have some fundamental limitations including size and density of the nozzle array, and ejection frequency, both primarily due to thermal problems. Mechanical jetting has limits in the density of the nozzle array, while the ejection frequency is limited by physical properties, and jetting reliability limited due to the difficulty of fabrication.

On the other hand, electro-hydrodynamic jet printing [4,6], or electrostatic field induced jetting device [5], based on the direct manipulation of liquid by an electric field, appears more promising. Using a continuously focused colloid jet, Lee, et al. [6] have introduced the electro-hydrodynamic printing of silver nano-particles as a direct writing technology. Park, et al. [4] have been able to use electro-hydrodynamic spraying to print images and electrode structures from gold of line width ~2μm. Such structures may be used in the manufacture of circuitry. Lee, et al. [5] have developed an electro-spray nozzle specifically for drop-on-demand inkjet printing. Their design has been able to provide relatively stable and sustainable droplet ejections under a wide variety of applied voltages. They showed successfully the feasibility of the electrostatic force to eject liquid droplet for the application to industry. However their technology should be extended to multi-nozzle device which can be manufactured massively and reproduced with appropriate yield.

Hyrdophobicity of a given surface is known to enhance the stability of a liquid meniscus in contact with that surface, and hence the stability of a cone-jet [11]. However, even on a hydrophobic surface against which a meniscus has a contact angle of around, a cone-jet is not stable and the meniscus on top of the nozzle may overflow onto the surrounding surface. We need to produce a jetting nozzle that can eliminate these instabilities during jetting. This objective is most readily achieved by fabricating some sort of protruding nozzle; however, a protruding nozzle is difficult to manufacture.

Thus, we realize that a flat nozzle composed of a super-hydrophobic material (that is, with a static contact angle greater than 150°[12]) is the most advantageous, as the resulting high-contact angle of the liquid meniscus at the nozzle's opening diminishes potentially hazardous leaks to the nozzle's surface and thus ensures long term stability and repeatability of the electro-spray process.

A known process for creating a super-hydrophobic surface is ion beam treatment [13]. The efficacy of the ion beam in modifying the topology and wetting characteristics of polymer surfaces has been established [14]. Capps, et al. [15] have reported on the effectiveness of argon and argon-oxygen ion beams on polyfluorotetraethylene (PTFE) in particular.

In this article, in order to fabricate polymer based electro-spray device with super hydrophobic nozzle, we use Teflon AF (amorphous fluoropolymers) 1600 and PTFE (polyfluorotetraethylene) plate with ion beam treatment to fabricate the super-hydrophobic surface.

2 FABRICATION OF SUPER-HYDROPHOBIC SURFACE

2.1 Ion beam treatment experiments

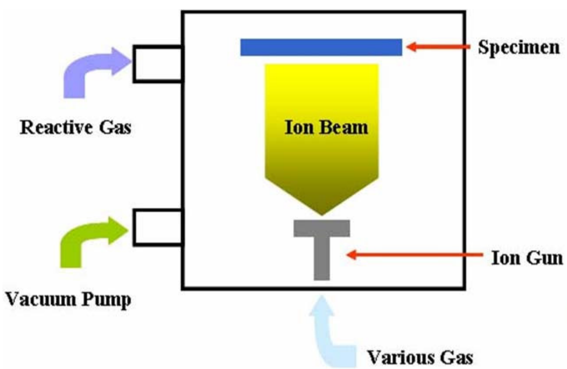

Fig1. Ion beam treatment equipment

To fabricate super-hydrophobic surface we use ion beam treatment process as shown in Fig. 1. Argon and oxygen are supplied to a vacuum chamber and then plasma ion beam is created and bombards polymer surface. In order to obtain the super-hydrophobic surface, the optimal conditions of modification were examined varying argon and oxygen concentration and energy levels. In this study we use Teflon AF 1600 and PTFE. Teflon AF 1600 is coated on a substrate and treated by 1.5 keV ion beam made from argon 3 sccm and oxygen 3 sccm gases. And PTFE is treated under the condition of argon 2 sccm and oxygen 2 sccm, and 1.5 keV.

2.2 Contact angle measurements

Contact angles of 2μl DI water droplet is measured on the treated surface using CCD camera and X-Y stage to investigate the effects of exposure time and energy level.

Figure 2 shows the shows the contact angle results of treated Teflon surface. Because the thickness of the Teflon layer affects much a super-hydrophobic surface characteristic, we tested several Teflon layers varying the spin coating speed from 350 rpm to 1000 rpm. In the case of 350 rpm, Teflon layer thickness is around 5 μm, which is measured by alpha step machine. For 700 rpm and 1000 rpm the thickness is measured to be around 3 μm. Contact angle could be lager than 150° when the exposure time is 5 min for the layer by 350 rpm spin coating, while the others show lower contact angle (nearly 100°) after 5 min. This observation depicts that 3 μm layer of Teflon is not enough to generate super0hydrophobic surface. The Teflon layer should be etched to form microscale structures on the surface by means of ion beam. Therefore, if the thickness of the layer is thin, the micro-structured Teflon surface may be too much.

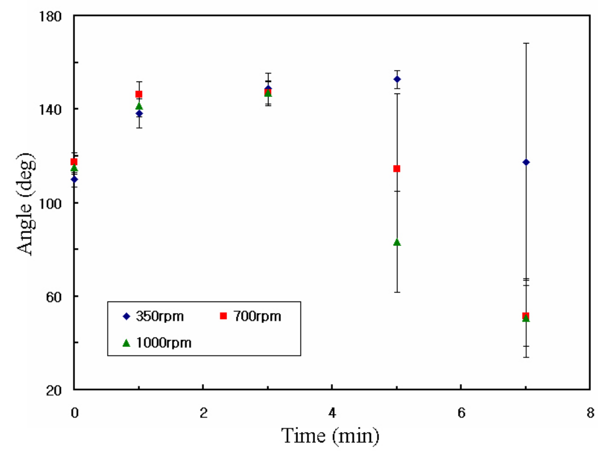

Fig2. Treated Teflon layer contact angle results

Figure 3 shows the contact angle results of treated PTFE surface and degradation characteristics are observed during longer than 2 months. Ion beam treated PTFE surface, hydrophobicity is increasd as expose time and contact angle is increased. First observation contact angle in July was 155°and after two month later, the contact angle did not change and kept same contact angle. With these results, PTEF surface can be treated permanent super-hydrophobic surface and can be applied to super-hydrophobic nozzle for electro-spray device.

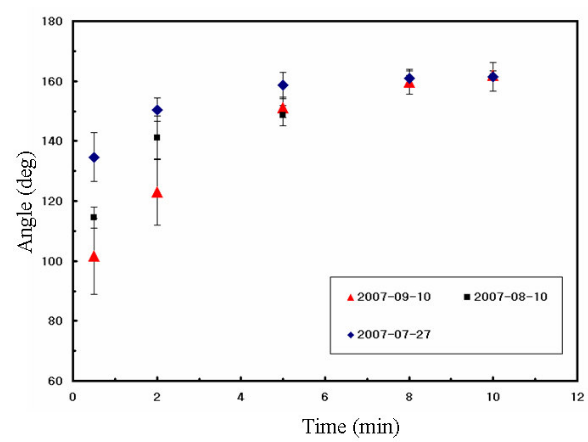

Fig3. Ion beam treated PTEF contact angle results

To try out quantitative data of nano structure after the ion beam treatment on the PTFE, we take AFM (atomic force microscope) and SEM (scanning electron microscope) data. Figure 4 show results of PTFE and treated PTFE surfaces. We see the width of the nano-scale structures is approximately 200nm and the height is 1.2µm, respectively. Due to these nano-scale structures, treated PFTE surface can enhance the liquid meniscus contact angles to super-hydrophobic ranges.

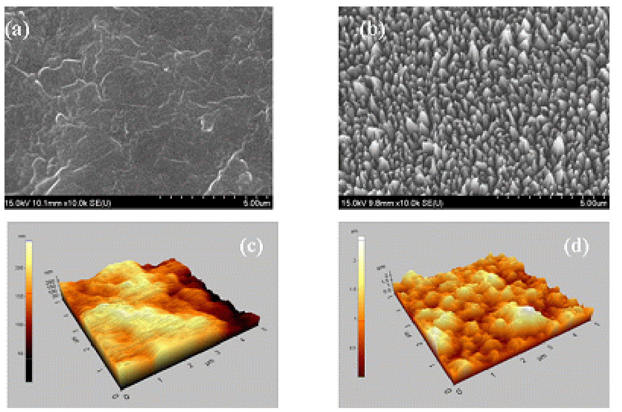

Fig4. SEM and AFM results. (a) and (c) PTFE, (b) and (d) treated PTFE

3 RESULTS AND DISCUSSIONS

3.1 Ion beam treated nozzle

To fabricate PMMA reservoir and PTFE plate nozzle (the nozzle diameter is 700µm), we used CNC machine and laser cutting machine. And this PTFE nozzle treated super-hydrophobic by ion beam for forming super-hydrophobic surfaces. The treated ion beam condition was Ar 2 sccm, O2 2sccm and 1.5kev.

The Al plate (thickness 0.2mm) is used for ground electrode, and using drilling machine fabricate the hole (hole diameter is 2mm). The gap between nozzle and ground electrode set up 3 mm. Using syringe pump delivered mixed solution. For solution, mixed D.I water 50%, methanol (CH_3OH) 49%, and acetone (CH_3COCH_3) 1%.

When high voltage supply, meniscus shape is changed Taylor-cone and tiny jet spread from the apex of the cone shape meniscus on the ion beam treated surface nozzle.

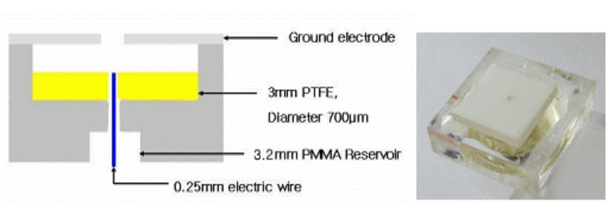

Fig5. The schematic of Ion beam treated surface PTFE nozzle.

3.2 Sequential elector-spray results

Figure 6 and 7 show the sequential images of electro-spray through hydrophobic PTFE nozzle as well as super-hydrophobic treated PTFE nozzle. For the PTFE nozzle, as the electro-spray operates repeatedly, the meniscus widely spreads around the nozzle and also shape of the meniscus changes to make the spray to be inefficient.

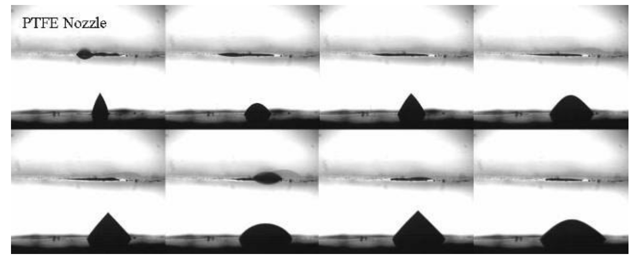

Fig6. The sequential images of Electro-spray on the PTFE surface nozzle. Flow rate is 5µl/min and operating voltage is 4.0kV.

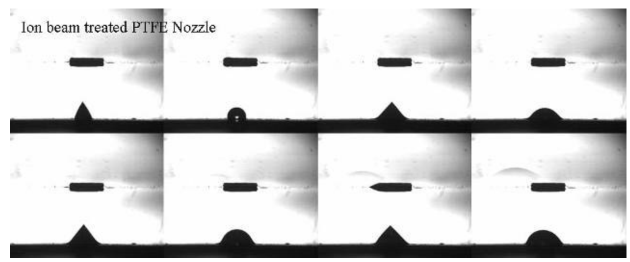

Fig7. The sequential images of Electro-spray on the Ion beam treated PTFE surface nozzle. Flow rate is 5µl/min and operating voltage is 4.0kV.

On the other hand, for the ion beam treated PTFE surface nozzle, as shown in Fig. 7, the liquid doesn't overflow and it keeps the same initial cone shape and position. Because of the super-hydrophobic surface, the liquid can be sustained to form a meniscus with high contact angle.

3.3 Electro-spray on the various nozzle

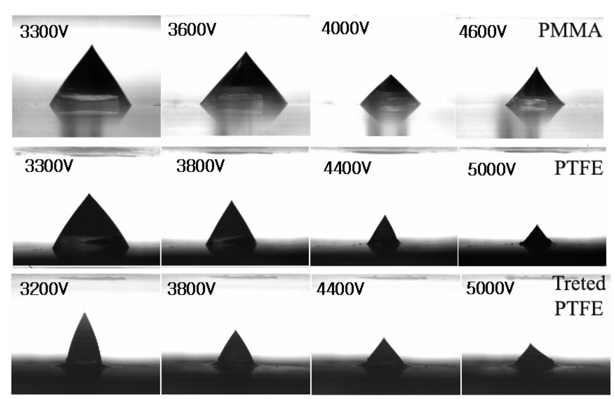

Fig7. Electro-spray through various nozzle

In case of PMMA nozzle, meniscus didn't keep the initial position and shape as increasing operating voltage. The PTFE nozzle case, at the low operating voltage range from 3.3kV to 3.8kV, liquid overflow so the meniscus width is larger than initial cone width.

But the Ion beam treated PTFE nozzle case, even at low operating voltage ranges; the meniscus width is nearly same with initial meniscus width. And as increasing voltage, the position of meniscus did not change.

According to these results, the super-hydrophobic surface nozzle is useful for forming cone jet spray and helpful to keep the initial cone shape and position also.

4 CONCLUSION

In this paper, to fabricate a super-ydrophobic surface, Teflon layer and PTFE (Polytetrafluoroethylene) plate are treated by argon and oxygen ion plasma beam. We vary argon and oxygen flow rate and energy level to investigate the effects of exposure time and energy level.

For the ion beam treated PTFE surface nozzle, the liquid does not overflow and keep the cone shape position even at the low voltage ranges. Because of the super-hydrophobic surface, the liquid can be sustained to form a meniscus with high contact angle. And the width of the meniscus at bottom is same as the nozzle diameter.

Using the ion beam treatment on PTFE surface, super-hydrophobic surface can be fabricated and allow the nozzle to keep the stable cone-jet even at the low voltage ranges.

5 ACKNOWLEDGEMENTS

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